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ABSORPTION AND RETENTION OF HYDROCYANIC ACID BY FUMIGATED FOOD PRODUCTS.

By E. L. GRIFFIN, *Assistant Chemist*, and I. E. NEIFERT, *Junior Chemist, Insecticide and Fungicide Laboratory, Miscellaneous Division, Bureau of Chemistry;* N. PERRINE, *Assistant in Plant Fumigation, Federal Horticultural Board*, and A. B. DUCKETT,[1] *Scientific Assistant, Stored-Product Insect Investigations, Bureau of Entomology.*[2]

CONTENTS.

INTRODUCTION.

Hydrocyanic acid, in the gaseous form, is used extensively in the United States as a fumigant for the destruction of insects and rodents, particularly the brown rat (*Mus norvegicus*). Probably the earliest recorded use of this gas for killing insects[3] was that by J. T. Bell (*4*),[4] who in 1877 employed it to rid an insect cabinet of insect pests. Credit is given to Dr. D. W. Coquillet for being the first to suggest the use of hydrocyanic acid gas for destroying insects on plants. In 1886, while employed as an agent of the United States Department of Agriculture, he began experiments with it which later showed its value for the destruction of scale insects infesting citrus trees (*14, 24*).

Since 1886 the use of hydrocyanic acid gas as a fumigant has been extended greatly, until it now includes the fumigation of dwellings, barracks, etc. (*12*), for the destruction of certain insects which are ordinarily classed as vermin, such as roaches, water bugs, and bedbugs, and the fumigation of warehouses and mills (*7, 8*) against certain insects that destroy food products. More recently this gas

[1] Deceased.

[2] H. L. Sanford assisted in the fumigation work and J. J. T. Graham assisted in making the analyses of the stored grains. As the plants and plant products coming in at the various ports of entry from foreign countries frequently are infested with insects new to the United States, E. R. Sasscer, entomologist in charge of the Plant Quarantine Service of the Federal Horticultural Board, outlined the fumigation procedure upon which the investigations herein reported were based, with the idea of determining whether or not various fruits, vegetables, and stored products fumigated with hydrocyanic acid gas in concentrations lethal to insects would be poisonous to consumers.

[3] Reference is made to the use of hydrocyanic acid gas generated rapidly by the action of sulphuric acid on potassium cyanide or sodium cyanide, and not to the use of potassium cyanide for killing insects in collectors' bottles, which probably is much the older practice.

[4] The numbers (italics) in parentheses throughout this bulletin refer to the bibliography on page 16.

has been employed at ports of entry (*9, 17*) to prevent the introduction from foreign countries of many injurious insect pests that have not yet gained a foothold here. Among the most important of these pests are the pink boll worm and the citrus black fly. Fumigation with hydrocyanic acid gas is also a means for the prevention of epidemics of yellow fever (*5*) and bubonic plague (*6, 13, 19*). Ships coming from ports where these diseases exist are fumigated on arrival in order to kill mosquitoes and rats which carry the causative organisms.

Food products fumigated to destroy the insects with which they are infested come into contact with hydrocyanic acid. This is true in the fumigation of imported fruits and vegetables at ports of entry and in the fumigation of flour and grains in mills and warehouses. In destroying insects and rats in dwellings and ships, foodstuffs may not be removed during exposure to the gas. In any case there is the possibility of exposure to the fumigant of products intended for food.

Since hydrocyanic acid is extremely poisonous to man, it is important to know how much of it is absorbed and retained by foods. Very little work on this subject seems to have been done, although apparently the opinion that there is no danger in the fumigation of dry foods[5] is fairly general.

REVIEW OF LITERATURE.

Guthrie (*10*) was unable to find a trace of residual gas in oranges that had been fumigated with hydrocyanic acid gas, in the proportions recommended for actual practice, for three hours and then allowed to remain in the open air for a half hour. He states that "similar experiments were made on samples of apples and lemons * * * with the same result."

Townsend (*22*) reports that seeds, whether dry or moist, are capable of absorbing hydrocyanic acid, even when its concentration in the atmosphere is very low. He fed fumigated seeds (corn and wheat) to mice and concludes from his experiments that "dry grains and other seeds treated for several days with hydrocyanic acid gas of any strength will not be injured for food. * * * Damp grains and other seeds treated with hydrocyanic acid gas of any strength, even for short periods of time, should not be used for food until several hours after removing from the gas."

Schmidt (*21*) fumigated peaches, plums, pears, lemons, and apples with hydrocyanic acid gas, apparently in rather high concentration. He placed his material in a chamber of 9.4 liters capacity and, in the course of a half hour, carried over into it by means of a stream of air the acid freed from 20 grams of potassium cyanide. He gives no values for the rate at which the air entered. If the stream of air was just strong enough to get all the hydrocyanic acid over into the chamber, without carrying any out, the atmosphere surrounding the fruit would contain about 78 per cent of the fumigant. This is equivalent to treatment with the gas from 213 ounces of potassium cyanide or 160 ounces of sodium cyanide per hundred cubic feet, which would be from 50 to 150 times as concentrated as that used

[5] H. D. Young reports that the workmen engaged in citrus fruit fumigation in California often hang their lunches in the trees which they expect to finish about lunch time. Immediately after fumigation the lunches are removed and eaten with no ill effects.

in practice. Schmidt probably did not get as high a concentration as this, but it must have been very high. This idea is strengthened by the fact that he reports marked physical effects on his fruits. Some of his results are shown in Table 1.

TABLE 1.—*Hydrocyanic acid on fumigated fruits* (*Schmidt*).

Fruit.	Length of time fumigated.	Hydrocyanic acid present.	
		After ½ hour.	After 48 hours.
	Hours.	*Per cent.*	*Per cent.*
Peaches	2	0.33	0.05
Do	½	.06	.02
Plums	½	.04	.006
Do	20	.03	[1] .008
Pears	½	.02	.005
Do	20	.02	[2] .008
Apples	½	.01	.002
Do	24	.16	.08
Lemons	½	.003	....
Do	20	.07	[3] .016

[1] 24 hours. [2] 5 days. [3] 14 days.

Schmidt found that peaches which had been fumigated for 18 hours gave off enough hydrocyanic acid to kill mice which were put in a jar with the fruit. He concludes that all fruits take up gaseous hydrocyanic acid and that certain fruits, for example peaches, take up the gas from even a very dilute atmosphere of it, so that it is possible that eating such fruit may cause some injury to health.

Quaintance (*18*) believes that very little, if any, gas is taken up by apples during fumigation with hydrocyanic acid. He and his associates have eaten freely of fumigated fruit, sometimes within 30 minutes of its removal from the fumigation box. These apples, of course, were first wiped.

Roberts (*19*) states that hydrocyanic acid fumigation does not injure any ordinary article of cargo.

Howard and Popenoe (*12*), in describing the method of fumigation against household insects, say "Liquids or moist foods, as milk, meat, or other larder supplies that are not dry and might absorb the gas, should be removed from the house." The inference is that other foods will not absorb enough of the fumigant to be dangerous. Their statement is apparently not based upon experimental evidence.

Bail and Cancik (*3*) say that fluids and moist foods should not be left in rooms which are being fumigated. They state that Heymons (*11*) found that fumigated flour was unchanged and nonpoisonous and that they found the same to be true for bran. After fumigating a food warehouse it is recommended that the food shall be used only after airing and that grain be shoveled over several times.

Bail (*2*) reports that Herr Hofrat v. Zeyneck found that after fumigation with 1 per cent by volume of hydrocyanic acid gas (time not stated) raw meat (minced) contained 186 parts of hydrocyanic acid per million, even after airing for 10 hours, moist vegetables contained 90 parts per million after airing for 2 days, fine flour contained 45 parts per million after 10 hours, and bran contained 30 parts per million. He recommends that all foods, whether wet or dry, be removed before fumigation.

Investigators in the United States Public Health Service (*1*) fumigated bread and milk with hydrocyanic acid and then fed them to white mice. They found that "when exposed to the cyanide gas in the concentration usually advised for fumigating tight compartments" they "did not absorb or adsorb sufficient cyanide to cause symptoms when fed to white mice." With double the amount of hydrocyanic acid, "prolonged" exposure, and no aeration after fumigation, death of the mice resulted, but "after one or two hours exposure of the food to the air no symptoms were produced." They summarize, "The conclusion from these experiments is that the possibility of food poisoning occurring from food materials exposed to cyanide gas is extremely remote."

Lubsen, Saltet, and Wolff (*15*) state that hydrocyanic acid can be used for the destruction of insects in flour and other foodstuffs, since it does not affect foods, except milk and other liquids.

Marchadier, Goujon, and de Laroche (*16*) advise against the use of hydrocyanic acid fumigation for flour. They recognize its value for clothes and things of that type, but think that flour may hold enough of the gas to cause injury to health. They found a hydrocyanic acid content of 82 parts per million in one flour and say that the foods prepared from it (cakes, sauces, etc.) still had the taste of cherry laurel, even after cooking. They do not describe the treatment which the flour had received.

PURPOSE OF PRESENT INVESTIGATION.

There are no analytical data on the quantity of hydrocyanic acid absorbed under the usual conditions of fumigation, except those of Guthrie and of Bail, who give some results on five products, but none which indicate the rate of loss of hydrocyanic acid on aeration. Schmidt worked with excessive concentrations of the fumigant.

Experimental work was therefore undertaken in the United States Department of Agriculture to find how much hydrocyanic acid is absorbed under ordinary conditions of fumigation on a large number of fruits, vegetables, and seeds, and at what rate it is given off when the products are exposed to the air.

EXPERIMENTAL WORK.

FRUITS AND VEGETABLES.

Fruits and vegetables were bought in season in the open market and in a condition as nearly perfect as possible. They were divided into three lots.

One lot was analyzed without being fumigated, to guard against reporting as absorbed hydrocyanic acid any which might be present in the fruit naturally.

The second lot was fumigated at normal atmospheric pressure (NAP) by the "pot" method. The fumigant in this method was prepared by adding sodium cyanide to diluted sulphuric acid in the proportion of $1:1\frac{1}{2}:2$. That is, for every avoirdupois ounce of sodium cyanide $1\frac{1}{2}$ fluid ounces of sulphuric acid and 2 ounces of water are used.

The third lot was fumigated by a modification of the vacuum method described by Sasscer and Hawkins (*20*). The fumigant in this method was prepared from sodium cyanide, sulphuric acid, and

water in the proportion of $2\frac{1}{2}:1:1$. That is, for every $2\frac{1}{2}$ fluid ounces of cyanide solution,[6] 1 fluid ounce of acid and 1 fluid ounce of water are used. The procedure is as follows: The material to be fumigated is placed in the fumigation chamber, in this case a horizontal iron retort with a capacity of 100 cubic feet, and the door is closed and clamped. The air is exhausted until the gauge registers 26 inches. At this stage the gas is generated by introducing into the generator the chemicals in the following order: Water, acid, cyanide in solution. The valve separating the generator from the fumigation chamber is opened, and the cyanide solution is allowed to flow slowly into the diluted acid in the generator. When all the cyanide solution has entered, the outside valve of the generator is opened, and the air is allowed to wash all of the gas over into the fumigation chamber. After washing for 5 minutes the vacuum in the fumigatorium is completely broken. The material is exposed to the gas for a period of time equal to 1 hour from the time the cyanide solution started to flow into the generator. To remove the gas-air mixture at the end of the exposure period, the fumigation chamber should be pumped to a vacuum of 25 inches. The valves of the chamber are then opened and the vacuum is broken. The chamber is opened and the material to be analyzed is removed.

Commercial 96–98 per cent sodium cyanide, usually at the rate of 4 ounces per hundred cubic feet of fumigated space, was used in this work, and the gas formed from it when treated with commercial 93 per cent sulphuric acid was allowed to remain in contact with the product for the time indicated. Even this dosage is higher than that now used in practice, usually $1\frac{1}{2}$ to 2 ounces of sodium cyanide per hundred cubic feet.

The temperature and humidity were accurately determined and recorded in each case.

Part of the material was analyzed immediately after fumigation, and part of it was stored in the refrigerator for 24 hours before being analyzed. Material which is usually pared before consumption was pared and separate analyses were made on the rind and flesh.

Hydrocyanic acid was determined, after distillation with tartaric acid, by the method of Viehoever and Johns (*23*). The results of these experiments are shown in Table 2.

TABLE 2.—*Hydrocyanic acid in fruits and vegetables after fumigation.*[1]

Product.	Sodium cyanide.		Temperature.	Relative humidity.	Period after fumigation.	Hydrocyanic acid in—		
	NAP	Vac.				Whole fruit.	Rind.	Flesh.
	Oz. per 100 cu. ft.	*Oz. per 100 cu. ft.*	*° F.*		*Days.*	*Parts per million.*	*Parts per million.*	*Parts per million.*
Apples:								
Ripe	......	4	64	43	1	[2] 3	......	......
Do	......	4	64	43	2	5	......	......
Do	......	2	75	51	0	42	......	......
Do	......	2	75	51	0	36	......	......
Do	4	......	72	33	0	......	7	6
Do	4	......	72	33	1	......	6	2
Do	......	4	74	23	0	......	97	42
Do	......	4	74	23	1	......	16	5

[1] All samples were exposed to the fumes for 1 hour, with the exception of the first pineapple sample, which was exposed for 70 minutes.
[2] Sample cut and allowed to stand overnight before analysis.

[6] This is made by dissolving sodium cyanide in water at the rate of 200 pounds to 50 gallons.

TABLE 2.—*Hydrocyanic acid in fruits and vegetables after fumigation*—Continued.

Product.	Sodium cyanide.		Temperature.	Relative humidity.	Period after fumigation.	Hydrocyanic acid in—		
	NAP	Vac.				Whole fruit.	Rind.	Flesh.
	Oz. per 100 cu. ft.	*Oz. per 100 cu. ft.*	°*F.*		*Days.*	*Parts per million.*	*Parts per million.*	*Parts per million.*
Avocadoes:								
Underripe		4	73	48	0		1,090	220
Do		4	73	48	1		250	78
Do	4		73	48	0		270	150
Do	4		73	48	1		170	93
Overripe		4	75.5	72	0		77	60
Do		4	75.5	72	1		95	41
Do	4		75.5	72	0		73	11
Do	4		75.5	72	1		75	41
Bananas:								
Ripe		4	64	43	2	20		
Do		2	75	51	0	80		
Do		2	75	51	0	95		
Do		4	73.5	40	0		440	110
Do		4	73.5	40	1		97	33
Do	4		73.5	40	0		210	61
Do	4		73.5	40	1		110	43
Beans, string (green):								
Fresh		4	77.5	43	0	1,100		
Do		4	77.5	43	1	280		
Do	4		77.5	43	0	480		
Do	4		77.5	43	1	440		
Beets:								
Good		4	64	42	0	130		
Do		4	64	42	0	160		
Do		4	67	53	0	49		
Do		4	67	53	1	57		
Do	4		67	53	0	54		
Do	4		67	53	1	49		
Cabbage:								
Good		4	64	42	0	220		
Do		4	64	42	0	240		
Do		4	67	39	0	190		
Do		4	67	39	1	54		
Do	4		67	39	0	160		
Do	4		67	39	1	39		
Carrots:								
Good		4	65	44	1	100		
Do		4	65	44	1	52		
Do		4	60	20	0		170	56
Do		4	60	20	1		120	44
Do	4		60	20	0		200	70
Do	4		60	20	1		150	80
Celery:								
Damp		4	65	44	0	300		
Do		4	65	44	0	310		
Do		2	75	51	0	190		
Fairly dry		4	67	39	0	120		
Do		4	67	39	1	75		
Do	4		67	39	0	74		
Do	4		67	39	1	70		
Corn, green, sweet:								
Fresh		4	82	65	0	230		
Do		4	82	65	1	150		
Do	4		82	65	0	430		
Do	4		82	65	1	380		
Cucumbers:								
Good		4	64	42	0	110		
Do		4	64	42	0	150		
Do		4	75.5	72	0		250	89
Do		4	75.5	72	1		58	17
Do	4		75.5	72	0		110	98
Do	4		75.5	72	1		120	45
Dasheen, small corms:								
Good		4	65	44	1	12		
Do		4	65	44	1	6		
Dasheen, large corms:								
Good		4	65	44	1	12		
Do		4	65	44	1	8		
Dasheen, tubers:								
Good		4	63	19	0		15	Trace.
Do		4	63	19	1		15	None.
Do	4		63	19	0		13	None.
Do	4		63	19	1		13	None.

TABLE 2.—*Hydrocyanic acid in fruits and vegetables after fumigation*—Continued.

Product.	Sodium cyanide.		Temperature.	Relative humidity.	Period after fumigation.	Hydrocyanic acid in—		
	NAP	Vac.				Whole fruit.	Rind.	Flesh.
	Oz. per 100 cu. ft.	*Oz. per 100 cu. ft.*	*°F.*		*Days.*	*Parts per million.*	*Parts per million.*	*Parts per million.*
Eggplant:								
Ripe		4	78	71	0		50	54
Do		4	78	71	1		44	61
Do	4		78	71	0		37	43
Do	4		78	71	1		42	42
Grapes (Worden variety):								
Ripe		4	82	65	0	430		
Do		4	82	65	1	230		
Do	4		82	65	0	420		
Do	4		82	65	1	130		
Grapefruit:								
Ripe		4	64	53	2	2		
Do		2	75	51	0	20		
Do		2	75	51	0	7		
Do		4	73.5	40	0		62	2
Do		4	73.5	40	1		50	12
Do	4		73.5	40	0		62	2
Do	4		73.5	40	1		35	7
Lemons:								
Ripe		4	64	53	2	41		
Do		2	75	51	0	120		
Do		2	75	51	0	88		
Overripe		4	73	55	0		230	21
Do		4	73	55	0		220	22
Do		4	73	55	1		160	14
Do		4	73	55	1		120	9
Ripe	4		74.5	58	0		290	11
Do	4		74.5	58	0		350	10
Do	4		74.5	58	1		110	17
Do	4		74.5	58	1		120	11
Lettuce:								
Damp		4	65	44	0	390		
Do		4	65	44	0	270		
Fairly dry		4	67	39	0	270		
Do		4	67	39	1	49		
Do	4		67	39	0	200		
Do	4		67	39	1	41		
Mameyea (*Lucuma mammosa*):								
Green		4	78	71	0		48	Trace.
Do		4	78	71	1		23	5
Green (soft)	4		78	71	0		54	4
Do	4		78	71	1		11	None.
Mammee apple (*Mammea americana*):								
Ripe	4		77.5	43	0		150	20
Mango (*Mangifera indica*):								
Green (soft)		4	78	71	0		140	76
Do		4	78	71	1		64	16
Green (firm)	4		78	71	0		140	32
Do	4		78	71	1		80	17
Muskmelon:								
Ripe		4	79	66	0		68	22
Do		4	79	66	1		54	28
Do	4		79	66	0		63	5
Do	4		79	66	1		70	21
Onions:								
Good		4	64	42	0	29		
Do		4	64	42	0	20		
Prime		4	78	71	0	Trace.		
Do		4	78	71	1	None.		
Do	4		78	71	0	Trace.		
Do	4		78	71	1	None.		
Oranges (Cuban) (Florida):[3]								
Good	1				5		None.	None.
Prime	1				5		None.	None.
Ripe		4	64	43	2	39		
Do		2	75	51	0	29		
Do		2	75	51	0	12		
Nearly ripe		4	73	55	0		240	11
Do		4	73	55	0		240	7
Do		4	73	55	1		110	11
Do		4	73	55	1		100	11
Ripe	4		74.5	58	0		110	3
Do	4		74.5	58	0		100	3
Do	4		74.5	58	1		94	4
Do	4		74.5	58	1		87	4

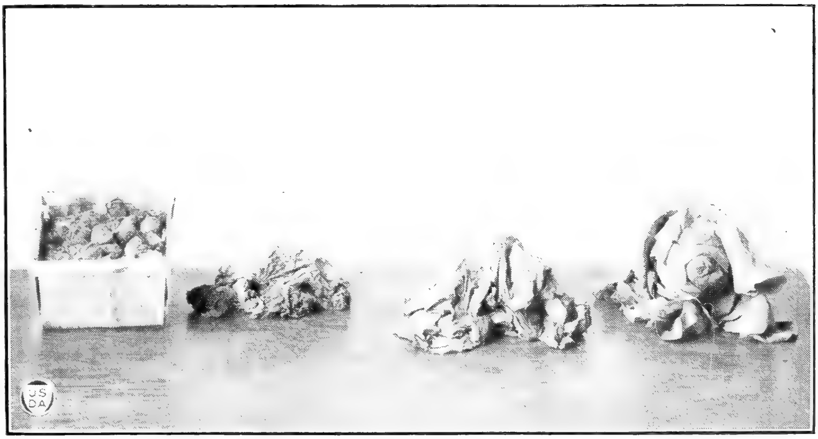
[3] Fumigated at Key West, Fla.

TABLE 2.—*Hydrocyanic acid in fruits and vegetables after fumigation*—Continued.

Product.	Sodium cyanide.		Temperature.	Relative humidity.	Period after fumigation.	Hydrocyanic acid in—		
	NAP	Vac.				Whole fruit.	Rind.	Flesh.
	Oz. per 100 cu. ft.	*Oz. per 100 cu. ft.*	*° F.*		*Days.*	*Parts per million.*	*Parts per million.*	*Parts per million.*
Parsnips:								
Good		4	60	20	0		280	88
Do		4	60	20	1		280	71
Do	4		60	20	0		230	85
Do	4		60	20	1		80	50
Peaches:								
Ripe		4	73.5	51	0		130	65
Do		4	73.5	51	1		52	32
Do	4		73.5	51	0		92	3
Do	4		73.5	51	1		130	12
Pears:								
Ripe		4	73.5	51	0		72	22
Do		4	73.5	51	1		18	11
Do	4		73.5	51	0		92	14
Do	4		73.5	51	1		16	3
Peas (green):								
Fresh		4	77.5	43	0		[4] 530	1,100
Do		4	77.5	43	1		[4] 130	520
Do	4		77.5	43	0		[4] 420	1,400
Do	4		77.5	43	1		[4] 230	200
Peppers (green):								
Fresh		4	82	65	0	370		
Do		4	82	65	1	220		
Do	4		82	65	0	320		
Do	4		82	65	1	120		
Pineapple (Red Spanish):								
Ripe		4	71	49	0	88		
Do		4	71	49	0	120		
Green		4	71	40	0		180	88
Ripe	2		71	49	0	60		
Do	4		71	49	0	59		
Do	2		71	40	0		100	14
Green	4		71	40	0		100	6
Do	1.5		70	70	1		23	6
Do	1.5		70	70	2		6	None.
Pineapples (Cuban): [3]								
Ripe (bulk)	1.08				7	None.		
Green (bulk)	1.6				6	[5] None.		
Do	1.27		84		4	[5] None.		
Ripe (bulk)	1.31		84		4	[6] None.		
Green (crated)	1.46		84		4	[7] None.		
Do	1.46		84		4	[8] None.		
Green (bulk)	1.37		86		3	[6] None.		
Do	1.02		90		3	[6] None.		
Plantains:								
Green		4	78	71	0		490	130
Do		4	78	71	1		130	56
Do	4		78	71	0		170	160
Do	4		78	71	1		140	50
Potatoes (sweet):								
Good		4	65	44	1	49		
Do		4	65	44	1	83		
Do	4		72	33	0		39	10
Do	4		72	33	1		21	2
Do		4	68	34	0		69	31
Do		4	68	34	1		82	21
Potatoes (white):								
Good		4	65	44	1	11		
Do		4	65	44	1	19		
Do	4		72	33	0		20	6
Do	4		72	33	1		8	2
Do		4	68	34	0		30	3
Do		4	68	34	1		8	1
Salsify:								
Good		4	64	42	0	200		
Do		4	64	42	0	190		
Fresh		4	63	19	0	110		
Do		4	63	19	1	49		
Do	4		63	19	0	110		
Do	4		63	19	1	54		

[3] Fumigated at Key West, Fla.
[4] Pod.
[5] 8 feet from generator.
[6] 6 feet from generator.
[7] 4 feet from generator.
[8] 14 feet from generator.

Before fumigation.



After fumigation.

EFFECT OF HYDROCYANIC ACID ON FUMIGATED PRODUCTS.

TABLE 2.—*Hydrocyanic acid in fruits and vegetables after fumigation*—Continued.

Product.	Sodium cyanide.		Temperature.	Relative humidity.	Period after fumigation.	Hydrocyanic acid in—		
	NAP	Vac.				Whole fruit.	Rind.	Flesh.
	Oz. per 100 cu. ft.	*Oz. per 100 cu. ft.*	*°F.*		*Days.*	*Parts per million.*	*Parts per million.*	*Parts per million.*
Sapodilla:								
Ripe	....	4	76.5	70	0	....	550	120
Do	....	4	76.5	70	1	....	110	34
Do	4	....	76.5	70	0	....	450	110
Do	4	....	76.5	70	1	....	50	15
Squash:								
Ripe	....	4	73.5	40	0	....	130	51
Do	....	4	73.5	40	1	....	110	15
Do	4	....	73.5	40	0	....	94	36
Do	4	....	73.5	40	1	....	55	29
Strawberries:								
Ripe but firm	....	4	75.5	89	0	53	....	....
Do	....	4	75.5	89	0	53	....	....
Do	....	4	75.5	89	1	54	....	....
Do	....	4	75.5	89	1	51	....	....
Do	4	....	75.5	89	0	34	....	....
Do	4	....	75.5	89	0	25	....	....
Do	4	....	75.5	89	1	55	....	....
Do	4	....	75.5	89	1	30	....	....
Tangerines:								
Ripe	....	4	64	43	1	[2] 4	....	....
Do	....	4	64	43	2	51	....	....
Do	....	4	74	23	0	....	400	59
Do	....	4	74	23	1	....	85	23
Do	4	....	74	23	0	....	430	54
Do	4	....	74	23	1	....	98	16
Tomatoes:								
Ripe	....	4	64	42	0	120	....	....
Do	....	4	64	42	0	89	....	....
Do	....	4	67	53	0	....	74	17
Do	....	4	67	53	1	....	28	23
Do	4	....	67	53	0	....	56	12
Do	4	....	67	53	1	....	14	9
Green	1¼	....	47	....	0	7	....	....
Do	1¼	....	47	....	1	2	....	....
Do	1¼	....	47	....	3	2	....	....
Do	1¼	....	70	....	0	[9] 2	....	....
Do	1¼	....	70	....	1	[9] 2	....	....
Do	1¼	....	70	....	3	[9] 2	....	....
Turnips:								
Good	....	4	65	44	1	120	....	....
Do	....	4	65	44	1	110	....	....
Do	4	....	72	33	0	....	120	53
Do	4	....	72	33	1	....	45	31
Do	....	4	68	34	0	....	340	120
Do	....	4	68	34	1	....	99	43
Watermelon:								
Fresh	4	....	79	66	0	....	5	None.
Do	4	....	79	66	1	....	4	None.

[2] Sample cut and allowed to stand overnight before analysis. [9] Sample stored at 70° F.

All the fumigated fruits and vegetables absorbed some hydrocyanic acid, but the quantities absorbed differed widely for different products. In general, the hard-skinned products, such as apples, oranges, lemons, watermelons, and grapefruit, had comparatively little of the gas in the flesh or edible parts. On the other hand, fruits and vegetables of a succulent nature or containing much chlorophyll absorbed larger quantities. Of course, in many cases these products are cooked before eating, so that most of the hydrocyanic acid, if not all, would have been driven off before they were eaten.

The physical effects on the products treated at the rate of 4 ounces of sodium cyanide per 100 cubic feet are noted in Table 3.

TABLE 3.—*Physical effects of hydrocyanic acid gas on fruits and vegetables.*

Product.	Effect of hydrocyanic acid.	Product.	Effect of hydrocyanic acid.
Apples	None.	Muskmelon	Decided softening.
Avocadoes	Deterioration very much hastened.	Onions	None.
Bananas	Slight yellowing of the pulp; some darkening of the epicarp.	Oranges	Do.
Beans (green, string).	None.	Parsnips	Do.
Beets	Do.	Peas	Do.
Cabbage	Some wilting and yellowing.[1]	Peaches	Do.
Carrots	None.	Pears	Darkening of the epicarp.
Celery	Severe wilting.[1]	Peppers (green)	None.
Corn (green, sweet)	None.	Pineapples	Do.
Cucumbers	Do.	Plantains	Decided softening of the pulp and browning of the epicarp.
Dasheen	Do.	Potatoes (sweet)	None.
Eggplant	Do.	Potatoes (white)	Do.
Grapes	Decided softening.	Salsify	Do.
Grapefruit	None.	Sapodilla	Do.
Lemons	Do.	Squash	Do.
Lettuce	Immediate and severe wilting.[1]	Strawberries	Decided softening and severe wilting.[1]
Mameyea	Softening.	Tangerines	None.
Mammee apples	None.	Tomatoes	Do.
Mango	Darkening of the epicarp.	Turnips	Do.
		Watermelons	Do.

[1] Deterioration was so serious that the product was not marketable.

Some of the fumigated products show a tendency to speedy decay, probably because of a reduction of their natural resistance to putrefactive organisms (Pl. I). This is particularly noticeable in the case of the avocado. Refrigeration does not seem to prevent the disintegration to any great extent.

No very direct relation seems to exist between the quantity of hydrocyanic acid absorbed and the damage to the tissues. Green peas and string beans both absorbed large quantities and yet showed no deterioration. On the other hand, mameyea, pears, and muskmelons contained comparatively small quantities but deteriorated greatly.

Although Schmidt (*21*) reports severe deterioration of peaches due to fumigation, the lower concentration of gas in the experiments here reported gave no such effects.

SEEDS AND FLOUR.

Experiments with seeds and flour were undertaken to determine the following points: (*a*) The quantity of hydrocyanic acid absorbed during fumigation; (*b*) the rate at which it is dissipated on storage; (*c*) the effect of evacuating the chamber several times after fumigation on the quantity of hydrocyanic acid retained by the product; (*d*) the relation of the concentration of the fumigant to the quantity absorbed.

Navy beans, white field corn, cowpeas, wheat, and flour were tested. Sacks containing about 15 pounds of each were fumigated with the dosage indicated, by a modification of the method of Sasscer and Hawkins (*20*).

In the first series of experiments the products were put into the fumigation chamber, and air was pumped out until the vacuum gauge registered 26 inches. The hydrocyanic acid gas was then introduced, allowing 5 minutes for generation and 5 minutes for washing the gas from the generator to the fumigation chamber, after

which the air was permitted to enter until normal atmospheric pressure had been attained. After the products had been exposed to the fumigant in this manner for an additional 50 minutes outside air was drawn over them for 10 minutes to remove the hydrocyanic acid. They were then taken from the chamber for analysis.

The treatment of the second series was conducted in the same manner as that of the first, except that at the completion of the 50-minute exposure the chamber was again evacuated until the gauge read 25 inches, air was introduced until atmospheric pressure was reached and, after a further 2-minute aeration, the products were withdrawn for analysis.

The treatment of the third and fourth series was the same as that of the second, except that the evacuation at the end was repeated once and twice, respectively, with intermediate aerations of 2 minutes in each case.

Determinations of hydrocyanic acid were made, after distillation with tartaric acid, by the method of Viehoever and Johns (*23*), on the day of fumigation (except in the first series) and at intervals thereafter. A delay with the first series made it impossible to conduct the analyses on the same day. The products were stored in a large, well-ventilated room during the intervals, at a temperature of about 70° F. The results of the examinations are recorded in Tables 4, 5, 6, 7, and 8.

TABLE 4.—*Hydrocyanic acid (parts per million) in fumigated navy beans.*

Sodium cyanide.	Number of times chamber was evacuated.	Hydrocyanic acid after—							
		0 day.	1 day.	4 days.	7 days.	14 days.	30 days.	60 days.	90 days.
Oz. per 100 cu. ft.									
1	0	....	3.3	3.3	1.7	0.8	None.	....	....
1	1	....	8.3	3.3	2.5	.8	None.	....	....
1	2	....	8.3	4.2	2.5	.8	0.8	0.4	0.4
1	3	....	....	3.3	1.7	.8	.8	.6	Trace.
2	0	20	4.2	2.5	1.7	1.2	1.2	1.2	1.2
2	1	16	8.3	6.6	2.5	1.7	1.2	1.2	.4
2	2	16	6.6	3.3	2.5	1.7	1.2	1.2	.4
2	3	12	3.3	3.3	3.3	2.5	.4	.4	.4
4	0	58	13	5.0	4.2	3.3	3.3	2.1	1.2
4	1	42	17	5.0	3.3	2.5	2.1	2.1	1.7
4	2	25	17	5.0	4.2	3.3	2.5	2.1	1.7
4	3	42	20	4.2	3.3	2.5	1.7	1.7	1.7
6	0	25	6.6	5.0	4.2	3.3	2.5	2.1	1.7
6	1	42	27	10	6.6	5.0	3.3	2.9	2.5
6	2	42	30	13	8.3	6.6	3.3	2.5	1.7
6	3	58	20	12	10	6.6	3.3	2.5	1.7

TABLE 5.—*Hydrocyanic acid (parts per million) in fumigated field corn.*

Sodium cyanide.	Number of times chamber was evacuated.	Hydrocyanic acid after—							
		0 day.	1 day.	4 days.	7 days.	14 days.	30 days.	60 days.	90 days.
Oz. per 100 cu. ft.									
1	0	....	7.5	2.5	1.2	None.	....	....	....
1	1	....	4.2	2.1	.8	None.	....	....	....
1	2	....	1.2	1.2	.8	None.	....	....	....
1	3	....	....	.8	.8	None.	....	....	....
2	0	62	5.8	1.7	1.7	1.2	1.2	0.8	0.8
2	1	25	8.3	3.3	1.7	1.2	1.2	1.2	.4
2	2	12	5.0	2.5	1.7	1.7	1.7	1.2	.8
2	3	8	5.0	2.5	1.7	1.7	1.2	1.2	.4
4	0	42	6.6	3.3	3.3	2.5	1.7	1.2	1.2
4	1	25	10	3.3	3.3	2.9	2.9	2.1	1.7
4	2	25	8.3	4.2	3.3	2.1	1.7	1.7	1.7
4	3	17	6.6	3.3	2.5	2.5	2.1	2.1	1.7
6	0	33	5.0	4.2	3.3	3.3	2.1	2.1	1.7
6	1	33	10	6.6	5.8	5.8	5.8	5.0	4.2
6	2	33	6.6	5.0	5.0	5.0	3.3	3.3	3.3
6	3	33	12	6.6	6.6	5.8	4.2	3.7	3.3

TABLE 6.—*Hydrocyanic acid (parts per million) in fumigated cowpeas.*

Sodium cyanide.	Number of times chamber was evacuated.	Hydrocyanic acid after—							
		0 day.	1 day.	4 days.	7 days.	14 days.	30 days.	60 days.	90 days.
Oz. per 100 cu. ft.									
1	0	....	6.2	4.2	3.3	2.5	1.7	1.2	1.2
1	1	....	16	5.0	4.2	2.5	2.1	1.7	1.7
1	2	....	4.2	4.2	4.2	2.5	1.7	.8	.8
1	3	....	....	4.2	4.2	1.7	1.2	.8	1.2
2	0	56	16	3.3	2.5	2.1	1.7	1.7	1.7
2	1	33	16	5.0	3.3	2.5	2.1	2.1	1.7
2	2	21	17	5.0	4.2	2.5	2.1	1.7	1.7
2	3	16	11	4.2	3.3	3.3	2.1	2.1	1.7
4	0	83	33	17	6.6	5.8	5.8	3.3	2.1
4	1	50	33	13	5.0	5.0	5.0	4.2	3.3
4	2	42	33	8.3	5.0	4.2	4.2	4.2	3.3
4	3	42	23	6.6	5.8	5.8	5.0	3.3	3.3
6	0	33	17	8.3	8.3	6.6	4.2	4.2	3.3
6	1	83	27	8.3	8.3	7.5	7.5	6.6	5.0
6	2	130	27	17	13	5.0	5.0	5.0	4.2
6	3	100	40	13	12	10	6.6	6.6	5.0

No hydrocyanic acid was found in unfumigated samples of any of the products, showing that none of it was naturally present in them.

All of the seeds absorbed hydrocyanic acid on fumigation. The results obtained on the day of fumigation have little comparative significance, since much of the gas was loosely held and variations of three or four hours in the times of standing were unavoidable. They show, however, that the quantity then present is fairly large. Most of it disappears during the first few days. In fact, in most cases the hydrocyanic acid content, on the fourth day, was not more than 5 parts per million. After this time there was an extremely slow dis-

TABLE 7.—*Hydrocyanic acid (parts per million) in fumigated flour.*

Sodium cyanide.	Number of times chamber was evacuated.	Hydrocyanic acid after—			
		0 day.	1 day.	4 days.	7 days.
Oz. per 100 cu. ft.					
1	0	....	None.	....	....
1	1	....	None.	....	....
1	2	....	None.	....	....
1	3	....	....	None.	....
2	0	50	2.5	None.	....
2	1	83	3.3	0.8	None.
2	2	83	8.3	None.	....
2	3	83	3.3	None.	....
4	0	33	None.	....	....
4	1	150	3.3	None.	....
4	2	50	4.2	None.	....
4	3	120	6.6	None.	....
6	0	100	3.3	.8	None.
6	1	170	6.6	.8	None.
6	2	200	8.3	.8	None.
6	3	170	3.3	None.	....

TABLE 8.—*Hydrocyanic acid (parts per million) in fumigated wheat.*

Sodium cyanide.	Number of times chamber was evacuated.	Hydrocyanic acid after—							
		0 day.	1 day.	4 days.	7 days.	14 days.	30 days.	60 days.	90 days.
Oz. per 100 cu. ft.									
1	0	....	5.0	3.3	2.5	1.7	1.2	1.2	1.2
1	1	....	4.2	3.3	2.5	1.7	1.7	1.7	1.7
1	2	....	4.2	3.3	2.5	1.7	1.7	1.2	1.7
1	3	....	....	2.5	2.5	1.7	1.7	1.7	1.7
2	0	17	8.3	3.7	3.3	2.5	2.1	2.1	2.1
2	1	21	6.6	5.0	4.2	3.3	3.3	2.1	1.7
2	2	13	5.0	3.3	2.5	2.5	2.5	2.1	1.7
2	3	13	3.3	3.3	3.3	3.3	2.9	2.9	2.1
4	0	17	6.6	6.6	5.0	4.2	4.2	4.2	3.3
4	1	25	6.6	5.8	4.2	4.2	3.3	2.9	2.9
4	2	17	6.6	5.0	4.2	4.2	4.2	4.2	3.3
4	3	17	8.3	6.6	4.2	4.2	4.2	3.3	2.9
6	0	17	5.0	3.3	3.3	3.3	2.5	2.9	2.5
6	1	25	6.6	5.8	5.8	5.8	5.0	5.0	4.2
6	2	33	6.6	6.6	5.0	5.0	4.2	4.2	3.3
6	3	25	6.6	6.6	5.8	5.8	4.2	4.2	3.3

sipation, a very small quantity of the fumigant being present at the end of the 3-month experimental period in all but a few cases.

The flour differed from the seeds in that, while it at first took up a large quantity of hydrocyanic acid, the union seems to have been extremely weak and by the end of four days, or, at most, a week, no traces of it could be found.

Evacuating the fumigation chamber once, twice, or three times to get rid of the fumigant did not have much effect. In fact, a sample from the series in which the chamber had been evacuated two or three times frequently had a higher gas content than the corresponding sample in the series in which the chamber had not been evacuated.

The quantity of sodium cyanide used had a marked effect on the hydrocyanic acid absorbed by the product. This effect was noticeable after storage for 3 months.

MISCELLANEOUS PRODUCTS.

In the work of the Department of Agriculture it has at times seemed desirable to fumigate certain other material with hydrocyanic acid. These products have been analyzed, with a view of determining their safety for use after fumigation. The results are shown in Table 9.

TABLE 9.—*Residual hydrocyanic acid in miscellaneous products after fumigation.*

Product.	Period after fumigation.	Sodium cyanide.	Exposure.	Pressure.	Hydrocyanic acid.
	Days.	*Oz. per 100 cu. ft.*	*Hours.*		*Parts per million.*
Beans, Brazilian	([1])	1	$1\frac{3}{4}$	Vac.[2]	Less than 4.
Beans, Dwarf	2	1	$1\frac{3}{4}$	Vac.	5
Cotton seed, Columbia:					
Whole seed	4	3	$\frac{3}{4}$	Vac.	58
Hulls	4	3	$\frac{3}{4}$	Vac.	110
Meats	4	3	$\frac{3}{4}$	Vac.	None.
Whole seed	4	6	$\frac{3}{4}$	Vac.	83
Hulls	4	6	$\frac{3}{4}$	Vac.	140
Meats	4	6	$\frac{3}{4}$	Vac.	None.
Cotton seed, Sea Island:					
Whole seed	4	3	$\frac{3}{4}$	Vac.	75
Hulls	4	3	$\frac{3}{4}$	Vac.	150
Meats	4	3	$\frac{3}{4}$	Vac.	None.
Cotton seed, Trice:					
Whole seed	4	3	$\frac{3}{4}$	Vac.	66
Hulls	4	3	$\frac{3}{4}$	Vac.	140
Meats	4	3	$\frac{3}{4}$	Vac.	None.
Whole seed	4	6	$\frac{3}{4}$	Vac.	83
Hulls	4	6	$\frac{3}{4}$	Vac.	150
Meats	4	6	$\frac{3}{4}$	Vac.	None.
Cottonseed cake:					
Do	1	2	1	NAP[3]	8
Do	3	2	1	NAP	6
Do	7	2	1	NAP	5
Cowpeas, Groit	2	1	$1\frac{3}{4}$	Vac.	66
Chestnuts:					
Whole	0	([4])	([4])	([4])	140
Shells	0	([4])	([4])	([4])	180
Meats	0	([4])	([4])	([4])	130
Honey:					
Capped	0	4	1	NAP	Trace.
Uncapped	0	4	1	NAP	9
Capped	1	4	1	NAP	None.
Uncapped	1	4	1	NAP	2

[1] Several.
[2] Vacuum fumigation by the method of Sasscer and Hawkins.
[3] Fumigation at normal atmospheric pressure.
[4] Unknown.

The hulls of the cotton seed and the shells of the chestnut absorb a large quantity of hydrocyanic acid. Unfumigated cottonseed hulls showed the presence of no hydrocyanic acid. Checks on the chestnuts were not available, but it does not seem possible that they would naturally contain such a large quantity. Hard rinds on fruits and vegetables tended to prevent absorption of the gas. No explanation is offered for this difference in behavior.

The absorption of hydrocyanic acid by uncapped honey was unexpectedly low. This was also surprising, in view of the fact that moist foods have a tendency to absorb the acid fairly rapidly.

SUMMARY.

Hydrocyanic acid gas, widely used as a fumigant against certain insects and rats, often comes in contact with materials intended for food. The quantity of hydrocyanic acid absorbed and retained by various fumigated foodstuffs has been determined.

All of the products examined absorbed the fumigant to some extent. Hard rinds of vegetables or skins of fruits had a tendency to decrease the absorption. Chlorophyll-bearing vegetables, or those of a succulent nature, in general, took up large quantities of hydrocyanic acid.

Some of the fruits and vegetables suffered physical injury (wilting, softening, or discoloration) because of fumigation to such an extent that they were unmarketable.

In the case of the seeds most of the hydrocyanic acid was rapidly dissipated, so that by the fourth day the content usually was not more than 5 parts per million. After this there was a slow dissipation, a very small quantity of the fumigant being present at the end of three months. The flour examined absorbed a large quantity of hydrocyanic acid but gave it off so rapidly that by the end of four days, or, at the most, a week, no traces of it could be detected.

Evacuating the chamber after fumigation was not effective in removing absorbed hydrocyanic acid.

The concentration of hydrocyanic acid gas used had, in general, a marked effect on the quantity absorbed by the product. This was noticeable even at the end of three months.

The quantities of hydrocyanic acid absorbed by various other products were determined also.

No conclusions as to the safety of fumigated foods for consumption are drawn in this bulletin. Chemical observations alone are included. Determinations of the quantities of hydrocyanic acid injurious to human health lie in the domain of the pharmacologist.

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